FURTHER REMARKS ON THE SECOND LAW OF THERMODYNAMICS IN GENERAL RELATIVITY

BY RICHARD C. TOLMAN

NORMAN BRIDGE LABORATORY OF PHYSICS, CALIFORNIA INSTITUTE OF TECHNOLOGY

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1. *Introduction.*—In a previous article[1] I have attempted an extension of thermodynamics to general relativity, and in following articles[2] have discussed certain applications of this extension. The postulate that was taken in this work as the analogue of the ordinary first law of thermodynamics was the same as the modified principle of the conservation of energy given by Einstein[3] as applying in the case of general relativity considerations. And in spite of the early criticisms of Einstein's principle, based on the fact that it could not be expressed in the form of a tensor equation, I feel that Einstein's treatment is now safely regarded as satisfactory, since the principle *is* expressible by an equation which is true for all sets of coördinates. The postulate, which was taken in the work as the analogue of the second law of thermodynamics, was however a new one and the main purpose of the present article is to present some further reasons which led me to the principle chosen.

In the previous article the new postulate was stated in the form which it takes when applied to an isolated finite system, and was justified by showing that it reduced to the ordinary second law in the limiting case of flat space-time, and by showing that it agreed with the principle of covariance because of its expression in tensor form. In the present article, however, the new postulate will be presented in the form which it takes when applied to a non-isolated infinitesimal system, and will be justified by showing that it can be regarded as a very natural result of generalizing the older thermodynamics. To do this we shall first obtain from the older thermodynamics an expression which embodies the results of the second law as applied to an infinitesimal four-dimensional region in flat space-time. Proceeding on the basis of the equivalence hypothesis we shall then regard this expression as true for an infinitesimal region even in curved space-time. And, finally, we shall generalize so as to put this expression in covariant form, and thus obtain the desired modification of the second law.

It will also be shown as a further justification that the new form of the second law leads to an expression for the entropy of a system in a stationary state, which agrees with what is to be expected on the basis of the usual relation between entropy and probability. And the article will in addition present an opportunity to make a number of incidental remarks which may be of a clarifying nature.

2. *Application of Ordinary Thermodynamics to an Infinitesimal Region.*—Let us first examine the application of the classical thermodynamics to an infinitesimal region in flat space-time, employing Galilean coördinates, x, y, z and t, corresponding to the line element

$$ds^2 = -dx^2 - dy^2 - dz^2 + dt^2. \tag{1}$$

If we consider the material contained in the infinitesimal spatial volume $\delta x \delta y \delta z$, it would seem to be the essence of the second law that the increase in the entropy of this region which occurs in a time interval δt should be equal to or greater than the entropy which is brought into the region during that interval by the actual convection of material or by the flow of heat. Hence, we may write as an expression of the requirements of the second law, the inequality,

$$\left(\frac{\partial \phi}{\partial t}\right) \delta x \delta y \delta z \delta t \geqq -\left\{\frac{\partial}{\partial x}(\phi u) + \frac{\partial}{\partial y}(\phi v) + \frac{\partial}{\partial z}(\phi w)\right\} \delta x \delta y \delta z \delta t + \frac{\delta Q}{T} \tag{2}$$

where ϕ is the density of entropy, u, v and w are the velocities of macroscopic flow at the point in question, and $\delta Q/T$ is the quotient of the heat entering the region in the time δt, divided by the temperature of the boundary.[4]

In accordance with the special theory of relativity, however, which holds in the limiting case of flat space-time, we may now transform equation (2) in the following manner. Since entropy is an invariant for the Lorentz transformation, entropy density will evidently be affected by the Lorentz-Fitzgerald factor of contraction ds/dt, in such a way that we may make the substitution

$$\phi = \phi_0 \frac{dt}{ds} \tag{3}$$

where ϕ_0 is the proper density of entropy referred to coördinates stationary with respect to the macroscopic velocity of the material, and ds refers to the macroscopic motion of the material. Furthermore, since heat and temperature have the same transformation factors, on the basis of the special theory, we may also introduce the substitution

$$\frac{\delta Q}{T} = \frac{\delta Q_0}{T_0}. \tag{4}$$

Making these substitutions, transposing terms, and writing explicit expressions for the components of velocity u, v and w, we may now rewrite (2) in the form,

$$\left\{\frac{\partial}{\partial x}\left(\phi_0 \frac{dt}{ds}\frac{dx}{dt}\right) + \frac{\partial}{\partial y}\left(\phi_0 \frac{dt}{ds}\frac{dy}{dt}\right) + \frac{\partial}{\partial z}\left(\phi_0 \frac{dt}{ds}\frac{dz}{dt}\right) + \frac{\partial}{\partial t}\left(\phi_0 \frac{dt}{ds}\right)\right\} \delta x \delta y \delta z \delta t \geqq \frac{\delta Q_0}{T_0} \quad (5)$$

and by cancellation, we obtain the symmetrical expression,

$$\left\{\frac{\partial}{\partial x}\left(\phi_0 \frac{dx}{ds}\right) + \frac{\partial}{\partial y}\left(\phi_0 \frac{dy}{ds}\right) + \frac{\partial}{\partial z}\left(\phi_0 \frac{dz}{ds}\right) + \frac{\partial}{\partial t}\left(\phi_0 \frac{dt}{ds}\right)\right\} \delta x \delta y \delta z \delta t \geqq \frac{\delta Q_0}{T_0} \quad (6)$$

3. *Generalization to Curved Space-Time and Curvilinear Coördinates.*—Expression (6) has been shown to be true in the limiting case of flat space-time using Galilean coördinates. Since it applies to an infinitesimal region in space-time, we shall now postulate, on the basis of the equivalence hypothesis, that it is also true for the case of curved space-time provided we use natural coördinates, and is a special case of a more general covariant expression true in all sets of coördinates.

A simple covariant expression of which (6) is a special case may now be obtained as follows. Let us define the *entropy vector* at the world-point in question by the equation

$$S^\mu = \phi_0 \frac{dx_\mu}{ds} \quad (7)$$

and the corresponding *entropy vector density* by the equation

$$\mathfrak{S}^\mu = S^\mu \sqrt{-g} = \phi_0 \frac{dx_\mu}{ds} \sqrt{-g}. \quad (8)$$

The desired generalized covariant expression may now be written in the form

$$\frac{\partial \mathfrak{S}^\mu}{\partial x_\mu} \delta x_1 \delta x_2 \delta x_3 \delta x_4 \geqq \frac{\delta Q_0}{T_0}. \quad (9)$$

To show that this expression is generally covariant, we note that it can be written, by a well-known transformation,[5] in the form

$$(S^\mu)_\mu \sqrt{-g}\ \delta x_1 \delta x_2 \delta x_3 \delta x_4 \geqq \frac{\delta Q_0}{T_0} \quad (10)$$

where $(S^\mu)_\mu$ is the contracted covariant derivative or divergence of S^μ. The quantities $(S^\mu)_\mu$ and $\sqrt{-g}\ \delta x_1 \delta x_2 \delta x_3 \delta x_4$ are however known to be invariants, while $\delta Q_0/T_0$ is obviously an invariant, so that both sides of expression (10) are tensors of rank zero, and the requirement of covariance is simply met.

To show that expression (9) reduces in the limit to the original expression (6), we note that in flat space-time using Galilean coördinates the quantity $\sqrt{-g}$ is a constant equal to unity. Substituting this value for $\sqrt{-g}$ in (8) and substituting the result into (9), we then easily obtain the earlier expression (6).

Hence the simple expression (9) is a natural covariant generalization of the requirements of the second law in flat space-time, and we shall assume it to be a correct statement of the general form of the second law.[6]

4. *Application to a Finite Isolated System.*—If we now integrate (9) over the whole of an isolated system and over any desired time interval, the summation of $\delta Q_0/T_0$ over the interior of the system will cancel out, since any heat entering a given element of volume is abstracted from neighboring elements. Hence for an isolated system we shall obtain the result

$$\int\int\int\int \frac{\partial \mathfrak{S}^\mu}{\partial x_\mu} dx_1 dx_2 dx_3 dx_4 \geqq 0. \qquad (11)$$

And this is the expression which was taken in the earlier work as a statement of the second law.

5. *Entropy of a System in a Stationary State.*—Let us now consider a system having the property that we can find some set of coördinates x_1, x_2, x_3, x_4 such that the velocities corresponding to the space-like coördinates will be everywhere equal to zero, in accordance with the equations

$$\frac{dx_1}{ds} = \frac{dx_2}{ds} = \frac{dx_3}{ds} = 0. \qquad (12)$$

For convenience we shall speak of such a system as being in a stationary state.

With these values for the spatial velocities, it is evident, from the equation of definition (8) for the vector density $\mathfrak{S}^\mu$, that the general expression (11) reduces to

$$\int\int\int\int \frac{\partial}{\partial x_4}\left(\phi_0 \frac{dx_4}{ds} \sqrt{-g}\right) dx_1 dx_2 dx_3 dx_4 \geqq 0 \qquad (13)$$

or, performing the indicated integration with respect to the time-like coördinates over an interval x_4 to x_4', we obtain

$$\left|\int\int\int \phi_0 \frac{dx_4}{ds} \sqrt{-g}\, dx_1 dx_2 dx_3 \right|_{x_4}^{x_4'} \geqq 0. \qquad (14)$$

And this expression can be conveniently transformed by using the general relation[7]

$$\sqrt{-g}\, dx_1 dx_2 dx_3 dx_4 = dV_0 ds \tag{15}$$

to give us

$$\Big| \int \phi_0 dV_0 \Big|_{x_4}^{x_4'} \geqq 0 \tag{16}$$

where dV_0 is the element of *proper* spatial volume, and the integration is to be taken over the whole of the isolated system.

We have thus obtained for such a system a simple quantity $\int \phi_0 dV_0$ whose value can only increase with the "time" x_4, and which hence might be called the entropy of the system. This quantity, however, is seen to be the summation, over the whole system, of the ordinary entropies of its parts, and by introducing for each of these parts the ordinary relation between entropy and probability

$$S = k \log W \tag{17}$$

and taking the probability of the arrangement of the total system as the product of the probabilities for each of its parts, we see that equation (16) also implies that the system could change with increasing values of x_4 only to arrangements of greater probability.

Thus, for a system "in a stationary state" we have obtained an additional justification for our generalized form of the second law.

6. *Incidental Remarks.*—In conclusion certain incidental remarks may be of interest.

In connection with the process of generalization by which we have passed from equation (6), valid in the special theory of relativity, to equation (9), valid in the general theory, it should be emphasized that equation (9) is in no sense strictly deduced from (6). Equation (9) may be regarded as a postulate from which (6) can be deduced as a special case, but not vice versa. It is of the essence of a real generalization that it should contain something not present in the special case which suggested it. Hence our postulate, equation (9), has not been proved necessarily true, but if true adds something genuinely new to theoretical physics.

With regard to the application of the second law to a finite isolated system as given in section 4, it should be noted that it is assumed as one of the characteristics of an isolated system, that no heat should cross the external boundary as measured by observers stationary with respect to that boundary.

In connection with the distinction between space-like and time-like coördinates made in section 5, and often arising in general relativity considerations, it is well to remember that the space-time manifold is best regarded not as four dimensional but rather as three-plus-one dimensional. In the case of the actual problems that have arisen in the field of general relativity, an examination of the line element involved always shows that one of the coördinates, say x_4, is distinguished by the fact that the corresponding component of the fundamental tensor, g_{44}, is always positive. This coördinate is the time-like one and the others space-like.

[1] Tolman, R. C., these PROCEEDINGS, 14 (1928), 268–72.

[2] *Ibid.*, 14 (1928), 348–53, and 14 (1928), 353–6.

[3] Einstein, A., *Berl. Ber.*, 1918, 448–59.

[4] It should be noted that what follows would not be affected if we took different temperatures for different parts of the boundary, and took $\delta Q/T$ as symbolic of a summation of such quantities for the different parts of the boundary.

[5] See Eddington, A. S., *The Mathematical Theory of Relativity*, Cambridge, 1923, equation (51.12).

[6] Equation (9) was presented by the author to the Astronomy Physics Club of Pasadena on March 2, 1928. It should be compared with equation (11) of M. Tu. De Donder, *Comptes Rend. Séance*, du 11, Juin, 1928, p. 1601.

[7] See Eddington, loc. cit., equation (49.42).

SERIES SPECTRA OF CADMIUM-LIKE ATOMS

By J. B. Green and R. J. Lang

Mendenhall Laboratory, Ohio State University and Physical Laboratory, University of Alberta

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The classification of spectra, homologous with that of cadmium, previously investigated by Green and Loring[1] and by Lang[2] has now been extended to Sb IV. The plates were taken and measured at the University of Alberta. A high potential spark in vacuum was used as a source.

The spectrum of Sb IV was classified in the usual way, by plotting the $\sqrt{\nu/R}$ values of the terms of Cd I, In II, and Sn III and extrapolating the curves thus found for each of the terms to Sb IV (a Moseley diagram). This is shown in figure 1. In this way we were enabled to find the approximate values of the terms of Sb IV and thus the approximate positions of the principal lines. In addition to this, the frequencies of lines corresponding to jumps between terms with the same principal quantum number increases uniformly in going from one element to the next. This corresponds to an assumption of the irregular doublet law of x-ray spectra, and is shown clearly in table 1.

Having determined the approximate positions of the groups, it was necessary to determine the multiplet separations. This was done by aid of the fourth power law (regular doublet law), assuming that this law